HYBRID TELLUROETHER LIGANDS AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES

by
RAMAN BATHEJA

A thesis submitted
in fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY

Department of Chemistry
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
JUNE 1995

DEDICATED TO
MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, ***"HYBRID TELLUROETHER LIGANDS AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES"***, being submitted by ***Mr. Raman Batheja,*** to the Indian Institute of Technology, Delhi, for the award of the degree of 'Doctor of Philosophy' in Chemistry, is a record of bonafide research work carried out by him. Mr. Raman Batheja has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

A K Singh
16.6.95

Dr. A.K. Singh
Department of Chemistry
Indian Institute of Technology
New Delhi - 110 016

ACKNOWLEDGEMENT

I extend my deep sense of gratitude to my supervisor, **Dr. A.K. Singh** for his advice, untiring efforts, constant inspiration and constructive criticism during the course of this investigation.

I am thankful to D.S.T., New Delhi and I.I.T., Delhi for financial assistance and Prof. G.N. Rao, Head, Department of Chemistry and Prof. B. L. Khandelwal for providing me the necessary research facilities.

My sincere thanks are due to all my laboratory collegues and friends especially Anup Madan, Anju Khanna, Vinod Srivastava, S. Modi, Tripat Pal Kaur Ramesh Kumari, V. Singh, Pramod Sharma, Sunil Kumar, Sandhya Jain, A. Das, Nidhi Arora, Kamini Uppal, Rajinder Kaur Bhatia, Abu Khalid, Satnam Singh, Kapil Dev, Reena Saxena and Pankaj Sharma for their help and moral support.

I would like to express my deep regards and thanks to my parents and brother for boosting my morale throughout the course of this work.

I am grateful to Mr. S. Ragothama, SIF, IISc Banglore for recording multinuclear NMR. I would also like to thank Mr. S. Guniyar, CDRI Lucknow, Mr. Avtar Singh, Punjab University Chandigarh, and Ms. Mamta, TIFR Bombay for recording NMR

I am also thankful to Mr. Naryan Singh (SLA) for his cooperation and help in the laboratory maintenance. The help rendered by the Instrument Laboratory and technical staff of the Department is highly appreciated.

Raman

(RAMAN BATHEJA)

ABSTRACT

Thirteen new polydentate organotellurium ligands bis(2-aminoethyl) telluride (**1**), bis(2-dimethylaminoethyl) telluride (**2**), bis(2-aminoethyl) ditelluride (**3**), bis(2-dimethylaminoethyl) ditelluride (**4**), 2-(dimethylaminoethyl)(4-methoxyphenyl)telluride (**5**), N,N,N',N'-tetrakis{2-(4-methoxyphenyl)telluroethyl}-ethane-1,2-diamine (**6**), 2-methoxyethyl(4-methoxyphenyl)telluride (**7**), bis{2-(4-methoxyphenyl)telluroethyl}ether (**8**), 1,2-bis{2-(4-methoxyphenyltelluro ethoxy)}ethane (**9**), 2-(phenyltelluromethyl)tetrahydro-2H-pyran (**10**), 2-(phenyltelluromethyl)tetrahydrofuran (**11**), 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxane (**12**), 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxolane (**13**) have been synthesized by reacting sodium aryltellurolate, Na_2Te and Na_2Te_2 with organic halides. The new diorganotellurides and ditellurides (**1-13**) have been characterized by elemental analyses, molecular weight, and conductance measurements, IR and NMR (^1H, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$) spectra.

The palladium and platinum(II) complexes of the types $[MCl_2(L)_2]$, $[M(L)_2](ClO_4)_2$, $[M(DPPE)(L)_2]$, $[M(PPh_3)_2(L)_2](ClO_4)_2$, $[M(Phen)(L)_2](ClO_4)_2$ (where M = Pd or Pt, phen = 1,10-phenanthroline, DPPE = 1,2-bis(diphenylphosphino)ethane and L = **10-13**) have been synthesized. UV-visible spectra of all five types of complexes indicate that the ligands constitute square planar geometry around Pd or Pt in all the cases. The complexes $[MCl_2(L)_2]$ behave as a non-electrolyte in acetonitrile and nitromethane solution and their IR spectra show only one ν(M-Cl) band suggesting the *trans* arrangement of ligands around Pd or Pt. The complexes $[M(L)_2](ClO_4)_2$, $[M(DPPE)(L)_2](ClO_4)_2$ and $[M(PPh_3)_2(L)_2](ClO_4)_2$ behave as a 1:2 electrolyte in

acetonitrile/nitromethane and $[M(Phen)(L)_2](ClO_4)_2$ in DMF. Molecular weights of these complexes except those of 1,10-phenanthroline have been found to be 1/3 of the expected value. Their IR spectra show bands around 620 and 1092 cm^{-1} characteristic of uncoordinated perchlorate ion supporting the conductance and molecular weight data. IR spectra of all the five types of complexes exhibit 10-15 cm^{-1} red shifted $\nu(Te\text{-}C_{aryl})$ vibrations. A band appearing around 330-440 cm^{-1} in the ligand **10** to **13** was red shifted (10-15 cm^{-1}) on complexation with Pd/Pt(II) indicating that it has some contribution from $Te\text{-}C_{alkyl}$ vibrations. The CH_2Te protons in ^1H NMR spectra of all these complexes undergo downfield shift (0.2 to 0.6 ppm) as compared to those of the ligands. Both these observations concur with the inference that ligation of **10** to **13** with palladium/platinum is through tellurium. ^1H NMR spectra of $[M(L)_2](ClO_4)_2$, the $-CH_2O-$ and $HCO-$ protons of the ring also undergo downfield shift (0.2 to 0.4 ppm) in contrast to those of $[MCl_2(L)_2]$. This observation suggests that in $[M(L)_2](ClO_4)_2$, **10** to **13** are ligating through oxygen alongwith tellurium.

In the $^{125}Te\{^1H\}$ NMR spectrum of each $[PtCl_2(L)_2]$ two signals in (1:5 ratio) observed downfield (120-158 ppm) in comparison to that of the corresponding ligand, indicate the presence of two isomers in solution. The signal appearing at higher frequency has been attributed to *trans* isomer (^1J(Pt-Te) 635-659 Hz). However, the satellite peaks of the signal appearing at lower frequency (*cis* isomer) were not observed due to its low intensity. Thus in solution $[PtCl_2L_2]$ type species exist as an isomeric mixture but in solid state *trans* form predominates and probably the isomeric inter-conversion in solution is quite fast. $^{125}Te\{^1H]$ NMR spectrum of each $[PdCl_2(L)_2]$ exhibit only one signal downfield (143-182 ppm) with respect to that of the ligand consistent with the formation of Pd-Te bond. IR spectra of these species show only one ν(Pd-Cl)

band around 340-350 cm^{-1} suggesting the *trans* arrangement of ligands around palladium.

The signals in $^{125}Te\{^1H\}$ NMR spectra of $[Pt(L)_2](ClO_4)_2$ (L = **10** and **11**) have been observed at further higher frequency (~113 ppm) in comparison to those of $[PtCl_2(L)_2]$. On contrary in ^{125}Te NMR spectra of $[Pt(\mathbf{12/13})_2](ClO_4)_2$ the signals appear relative to $[PtCl_2(\mathbf{12/13})_2]$ at lower frequency (13-15 ppm). These shifts can be explained on the basis of chelate effect. The ^1J(Pt-Te) values (688-704Hz) observed for $[Pt(L)_2](ClO_4)_2$ type of species are close to those reported for trans Te-Pt-Te system. Similarly in $^{125}Te\{^1H\}$ NMR spectra of $[Pd(\mathbf{10/11})_2](ClO_4)_2$ signals have been observed at further higher frequency (127-130 ppm) as compared to corresponding $[PdCl_2(L)_2]$ but in the spectra of $[Pd(\mathbf{12/13})_2](ClO_4)_2$ at a lower frequency (12-29 ppm) than those of $[PdCl_2(\mathbf{12/13})_2]$. These shifts can also be explained on the basis of chelate effect which is greater for five membered chelate rings of $[PdCl_2(\mathbf{10/11})_2]$.

The $^{31}P\{^1H\}$ NMR spectra of $[Pt(DPPE)(L)_2](ClO_4)_2$ comprise only one signal associated with ^{195}Pt satellites and ^1J(Pt-P) 2850-2885 has been found to be characteristic of P *trans* to Te ligand Thus these complexes seem to have essentially a structure in which two tellurium ligands are *cis* to each other. In $^{31}P\{^1H\}$ NMR spectrum of each $[Pd(DPPE)(L)_2](ClO_4)_2$ only one signal is observed in the range, δ, 42.4 to 43.9 ppm which is at 2-3 ppm higher frequency with respect to their platinum analogues. The chemical shift values in ^{31}P NMR of isostructural complexes of palladium(II) and platinum(II) with phosphine ligands differ in large number of cases by 2-3 ppm only, palladium showing at higher frequency than Pt. Therefore, $[Pd(DPPE)(L)_2](ClO_4)_2$ appears to be isostructural with its Pt analogues.

The $^{31}P\{^1H\}$ NMR spectra of $[(PPh_3)_2Pt(L)_2](ClO4)_2$ also display a single resonance signal with satellites due to Pt. The $^1J(Pt\text{-}P)$ values observed in the range 2990-3025 Hz, are characteristic of *trans* PPh_3-Pt-PPh_3 system. In $^{31}P\{^1H\}$ NMR spectra of $[Pd(PPh_3)_2(L)_2](ClO_4)_2$ also only one resonance signal has been observed in the range 20.15-20.96 ppm which is also at ~3 ppm higher frequency than their platinum analogues indicating that, the palladium and platinum complexes of this type are also isostructural.

The attempts to synthesize $[MClL_2]ClO_4$, $[M(DPPE)L](ClO_4)_2$, $[M(PPh_3)_2L](ClO_4)_2$, $[M(Phen)L](ClO_4)_2$ in pure form did not succeed. Similarly crystals of none of the above discussed complexes, suitable for X-ray diffraction could be grown.

The $[Pd(Phen)(L)_2](ClO_4)_2$ has been found to act as quencher for singlet oxygen generated in the presence of methylene blue, rose bengal and eosine as sensitizers. The reaction has been followed by monitoring the decrease in absorbance of ligand to ligand charge transfer (LLCT) band in visible region (440-454 nm) The quenching probably occurs through following mechanism:

$$^1S_0 \xrightarrow{h\nu} {}^1S_1$$

$$^1S_1 \xrightarrow{ISC} {}^3S_1$$

$$^3S_1 + {}^3O_2 \xrightarrow{ET} {}^1S_1 + {}^1O_2$$

$$^1O_2 \xrightarrow{K_d} {}^3O_2$$

$$^1O_2 + Q \xrightarrow{K_q} {}^3O_2 + Q^* \longrightarrow {}^3O_2 + Q$$

$$^1O_2 \xrightarrow{K_r} QO_2$$

It follows the kinetic equation 1

$$\log [Q] = -Kt + C \qquad (1)$$

(if $K_d >> (K_q + K_r)[Q]$; $K = I_{ab}\phi^1O_2 \frac{K_r}{K_d}$

where ϕ^1O_2 quantum yield of $^1O_2$ production and I_{ab} is intensity of absorbed light. The linear plots of log[Q] (or log A) vs irradiation times indicate that relative efficiencies for sensitizers are in the order :

methylene blue > rose bengal > eosin .

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